Gypsum wallboard as a sink for formaldehyde

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SUMMARY
Formaldehyde (HCHO) has been of special concern as an indoor air pollutant because of its presence in a wide range of consumer products and its adverse health effects. Materials acting as HCHO sinks, such as painted gypsum wallboard, can become emission sources. However, adsorption and desorption rate constants for HCHO have received little attention in comparison with the extensive sink effect studies for other volatile organic compounds (VOCs), especially the effects of humidity. To address this issue, small chamber tests were conducted to study the adsorption and desorption of HCHO by painted gypsum wallboard under different relative humidity conditions (20, 50, 70% RH) at 24 °C and one air exchange per hour. The concentration-time profiles from the tests are presented. The Langmuir isotherm model was used to estimate adsorption and desorption rate constants and to analyze the sink behavior. The results show that humidity impacts the adsorption and desorption of HCHO on painted gypsum wallboard. The amounts of HCHO adsorbed and desorbed were calculated. The discrepancy between the model predictions and experimental results implies that other factors, such as diffusion controlled process, may have contributed to the sink effect.

KEYWORDS
Adsorption, Desorption, Formaldehyde, Relative humidity, Building material

INTRODUCTION
Study of green materials and products is a rapidly growing field driven by concerns about increasing cost of energy consumption and the impact of the building environment on human health and performance. Formaldehyde (HCHO) has been of special concern because of its emissions from a wide range of products and potential health effects associated with the exposure to HCHO. Formaldehyde is released into homes from a variety of indoor sources (e. g., wood products, consumer products, tobacco products, and chemical reaction of ozone with indoor volatile organic compounds (VOCs) (LHSBC, 2007). Factors such as temperature, humidity, ventilation, and age of the house, etc., significantly affect HCHO levels indoors. Centers for Disease Control and Prevention (CDC) and Federal Emergency Management Agency (FEMA) announced that high levels of HCHO recently found in the FEMA trailers (U.S. HHS, 2007) were evidence of the need to understand the emission source, fate and transport of HCHO and reduce its emissions.

The sink effect, adsorption and desorption of organic compounds on interior surface, plays an important role in the indoor air quality (IAQ) measurements and predications (Hansson, 2003, and references therein). Materials, such as carpets and painted gypsum wallboard, which act as HCHO sinks, can become emission sources for years if humidity and temperature are changed. Little is known about the sink effect for HCHO, especially the effects of humidity.

Impact of relative humidity (RH) on HCHO source emissions and sink is an important consideration in green products research.

METHODS

Research has been conducted using 53 liter (L) stainless steel small chambers. The chambers were equipped with inlet and outlet manifolds for the air supply, temperature and relative humidity sensors, as well as data acquisition system. These chambers conform to ASTM D-5116-06. The test materials was gypsum wallboard painted with an interior latex paint (Eco Spec® Interior Latex Eggshell Enamel (223)) certified as meeting low emissions IAQ criteria. The formaldehyde emissions from this test material were shown to be low. For each test, two pieces (35 cm x 20 cm x 1.27 cm) of the gypsum wallboard were randomly selected from 49 pieces (from one sheet) and painted by following ASTM D6803-02. The edges of the boards were sealed with sodium silicate. The painted gypsum wallboards were placed under the ventilation hood and air dried for one week. A constant source of gas phase HCHO was generated using a permeation tube (Kin-Tek Laboratories, Inc.) in the 491M modular gas standards generation system (Kin-Tek Laboratories, Inc.). Nitrogen was used as the carrier gas at 100 to 200 mL/min depending on the designated RH. The nominal emission rate of HCHO was 3 μg/min and the concentration of HCHO delivered to the small chamber at one air exchange rate (ACH) per hour was about 3000 $\mu g/m^3$. The outlet of the gas standards generation system was wrapped with heating tape and controlled at 60 ºC. The small chamber temperature was about was controlled at 24ºC (±1 ºC) and air exchange rate was 1 ACH (±0.05 ACH).

The RH of the air supply to the 53-L stainless steel small chamber, housed in a temperature-controlled incubator, was controlled by blending dry and humidified air. A data acquisition system continuously recorded mass flow controllers' outputs, temperature, and RH in the chamber and inlet air. A 1 ½" computer cooling fan was placed in the chamber to insure good air mixing. Two pieces of wallboard were placed back to back vertically in the chamber with an exposed area of 1400 cm^2 and surface area/volume of 2.7 m^2/m^3. Empty chamber tests were performed as well. The surface-to-volume ratio for the empty chamber is 16.6 m^2/m^3. RH conditions for each of the tests are described in Table 1. Background samples were collected before the test specimens were placed into the chamber. Then source emission test was performed for 23 to 144 hours to determine the formaldehyde contribution of the sink source from the test specimens. During sink tests, gas phase HCHO was injected into the small chamber for 48 to 166 hours (the adsorption-dominated period) then the HCHO flow was disconnected from the chamber inlet and replaced by clean air for another 47 to 411 hours for desorption-dominated period. HCHO concentration was measured by collecting air samples on dinitrophenylhydrazine (DNPH) treated silica gel cartridges and analyzing by EPA method IP-6A.

To determine the amount of formaldehyde remaining in the test material after the small chamber sink test, the samples were removed from the chamber, sheared to 10 cm x 20 cm in size, and then placed in a high temperature chamber (HTC). The HTC was operated at 65 ºC to thermally desorb the remaining HCHO. The formaldehyde concentrations in the outlet air flow were monitored by collecting DNPH samples.

RESULTS AND DISCUSSION

Formaldehyde concentration time profiles were obtained. The results were evaluated by the first order reversible adsorption/desorption Langmuir-isothermal model and mass balance. Test data were also compared to a no-sink model. The Langmuir-isotherm model assumes a monolayer of molecules on a homogeneous surface with all adsorption sites independent and identical (Tichenor, et al. 1991). Thus at constant temperature, the VOC adsorption rate is proportional to the VOC concentration in the air and desorption rate is proportional to the mass of VOC adsorbed on the material surface.

$$\frac{dC}{dt} = \frac{R}{V} - NC - k_a CL + k_d ML \tag{1}$$

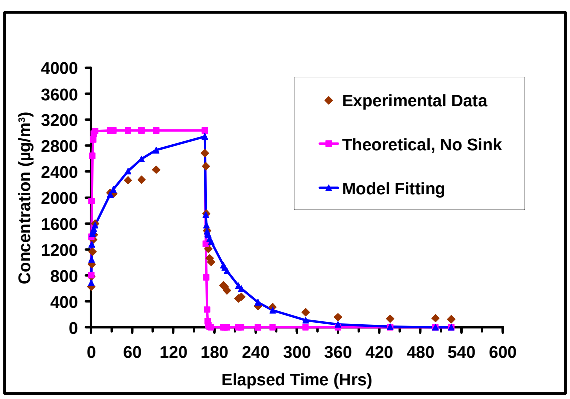
$$\frac{dM}{dt} = k_a C - k_d M \tag{2}$$

In the equations, C is the concentration of HCHO in the chamber air in mg/m^3, R is the constant emission rate of HCHO to the chamber in mg/h, V is the chamber volume in m^3, N is the air exchange rate in h^{-1}, k_a is the adsorption rate constant in m/h, k_d is the desorption rate constant in h^{-1}, L is the loading factor in m^{-1}, M is the mass of VOC adsorbed on the material surface in mg/m^2, t is the time in h. Using the Langmuir-isotherm equations, values of the constant k_a and k_d were obtained by least square fitting. The results obtained using MicroMath® SCIENTIST™ software and summarized in Table 1 show that under different RHs, sink effect of HCHO on stainless steel chamber can be neglected. Under 20% and 50% RH, adsorbtion and desorption behavior of HCHO on painted gypsum wallboard was very similar. However, the HCHO sorption capacity of painted gypsum wallboard at 66% RH appears to be about three to four times larger. The k_a/k_d ratios greater than10 suggests that painted gypsum board could be a significant sink for HCHO. R-squared as one of the statistical parameters used by SCIENTIST as an indicator of goodness-of-fit is also presented in Table 1. The k_a/k_d values of duplicate tests T3 and T4 estimate the precision of the tests.

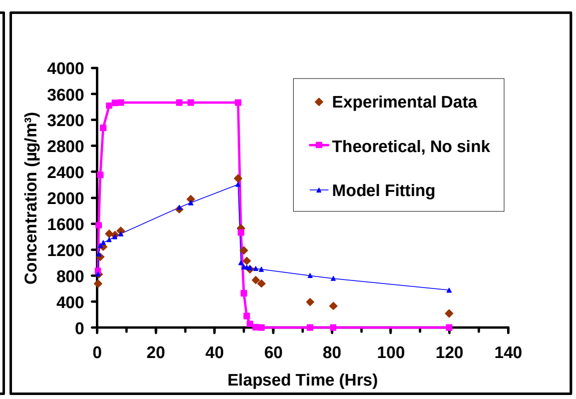
Table 1. k_a and k_d value of formaldehyde by MicroMath SCIENTIST software least square fit

Test ID	Materials	%RH	k_a (m/h)	k_d (h^{-1})	k_a/k_d	R-Squared
SCH-SE-ECH-T1	ECh [a]	51	1.6	103	0.02	0.9943
SCH-SE-ECH-T2	ECh	17	33	1732	0.02	0.9932
SCH-SE-ECH-T3	ECh	73	0.12	5.29	0.02	0.9888
SCH-SE-ECH-T4	ECh	72	0.03	3.61	0.01	0.9979
SCH-SE-WBC-T6	PGW [b]	21	0.52	0.03	16.0	0.9747
SCH-SE-WBC-T10	PGW	47	0.51	0.03	14.7	0.9846
SCH-SE-WBC-T11	PGW	45	0.42	0.04	10.9	0.9700
SCH-SE-WBC-T15c	PGW	66	1.0	0.03	40.0	0.9634

[a.] Ech is empty chamber. [b.] PGW is painted gypsum wallboard.



a)



b)

Figure 1. Langmuir-isotherm modeling of experimental data. a) SCH-SE-WBC-T11, 45% RH, b) SCH-SE-WBC-T15c, 66% RH.

Figure 1 presents the model predictions and experimental results. The discrepancy between the model predictions and experimental results implies that Langmuir-isotherm model may not be applicable when HCHO absorbed into the bulk of the material. Other factors, such as diffusion controlled process, may have contributed to the sink effect.

The overall mass balance for each wallboard test was calculated using:

$$M_{in} = M_{out} + M_{remain} + M_{on} \qquad (3)$$

where M_{in} is the total mass dosed into the chamber, M_{out} is the mass leaving the chamber, M_{remain} is the mass remaining in the chamber air, and M_{on} is the mass remaining on the surface of the material and diffused to the material interior. Mass balances are presented in Table 2. Comparison of mass balance among the three tests (SCH-T6, T10, T15C) with same amount of HCHO dosing and test conditions, showed that the overall missing mass is in the order of SCH-T6 (21% RH)< SCH-T10 (47% RH)< SCHT15 (66% RH). Test SCH-T11 was a similar test of SCH-T10 with an extended adsorption and desorption time periods.

Table 2. Mass balance calculation

Parameters				
Test ID	SCH-T6	SCH-T10	SCH-T11	SCH-T15C
%RH	21%	47%	45%	66%
Adsorption duration (hr)	47.9	47.2	166.7	48.2
Desorption duration (hr)	239.8	410.8	358.7	71.9
	Formaldehyde mass (mg)			
Total mass entered the chamber, M_{in}	8.72	9.91	36.03	10.17
Mass out of chamber during adsorption, M_{out-a}	5.13	5.45	20.82	4.89
Mass out of chamber during desorption, M_{out-d}	2.11	2.88	5.58	1.63
HTC thermal desorbed from tested material [a], M_{on}	1.05	0.64	1.36	1.52
Overall mass missing	0.43	0.94	8.29	2.13

[a.] Thermal desorption from "clean" gypsum board was measured (n=2) and subtracted from the mass desorbed from sink samples.

CONCLUSIONS

For the first time HCHO absorption rate constant k_a and desorption rate constant k_d values are obtained for painted gypsum wallboard under different RH values. The results shed light on the controlling mechanisms of painted gypsum wallboard as a sink for formaldehyde other than the first order reversible Langmuir-isotherm. The large k_a/k_d ratios (>10) imply that gypsum board can be a significant sink for formaldehyde. More studies are undergoing to identify those mechanisms.

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